

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Attorney Docket No.: 3081.117US01

Linde et al.

Confirmation No.: 9835

Application No.: 10/536,665

Examiner: Wong, Edna

Filed: May 27, 2005

Group Art Unit: 1795

For: PRODUCTION OF STRUCTURED CHROME LAYERS

---

DECLARATION PURSUANT TO 37 C.F.R. § 1.132

I, Rudolf Linde, declare under penalty of perjury that the following is true and correct to the best of my knowledge, information and belief:

1. I am a named inventor on the above-referenced patent application entitled "Production of Structured Chrome Layers." I have conducted five (5) comparative experiments to the claimed invention, which are summarized in below:

**Experiment 1 (according to Example 2 of the present U.S. application no. 10/536,665)**

A chromium electrolyte having the following composition was prepared:

Chromium acid anhydride ( $\text{CrO}_3$ ):	250 g/L
Sulphuric acid ( $\text{H}_2\text{SO}_4$ ):	2.5 g/L
Ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ ):	100 g/L
Methane sulfonic acid:	4 g/L
No fluorides added	

A piston ring was introduced into the electrolyte after conventional pre-treatment and electrolytically coated for 30 minutes at 55°C with a cathodic current yield of 11%. A structured hard chromium layer was obtained.

**Experiment 2 (according to Example A of Horsthemke et al. / US 6,837,981 B2, without F<sup>-</sup>)**

Chromium acid anhydride (CrO <sub>3</sub> ):	180 g/L
Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> ):	1.8 g/L (1 % of the chromic acid content)
Molybdic acid (MoO <sub>3</sub> , comm. grade, 85 %):	90 g/L
Methane sulfonic acid:	2.1 g/L
No fluorides added	

A piston ring was introduced into the electrolyte after conventional pre-treatment and electrolytically coated for 30 minutes at 55°C with a cathodic current yield of 16%. A non-structured hard chromium layer was obtained.

**Experiment 3 (according to Example A of Horsthemke et al. / US 6,837,981 B2, with F<sup>-</sup>)**

Chromium acid anhydride (CrO <sub>3</sub> ):	180 g/L
Sulphuric acid (H <sub>2</sub> SO <sub>4</sub> ):	1.8 g/L (1 % of the chromic acid content)
Molybdic acid (MoO <sub>3</sub> , comm. grade, 85 %):	90 g/L
Methane sulfonic acid:	2.1 g/L
Fluoride (F <sup>-</sup> ):	0.28 g/L

A piston ring was introduced into the electrolyte after conventional pre-treatment and electrolytically coated for 30 minutes at 55°C with a cathodic current yield of 16%. A non-structured hard chromium layer was obtained.

**Experiment 4**

A chromium electrolyte having the following composition was prepared:

Chromium acid anhydride ( $\text{CrO}_3$ ):	250 g/L
Sulphuric acid ( $\text{H}_2\text{SO}_4$ ):	2,5 g/L
Ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ ):	5 g/L
Methane sulfonic acid:	4 g/L
No fluorides added	

A piston ring was introduced into the electrolyte after conventional pre-treatment and electrolytically coated for 30 minutes at  $55^\circ\text{C}$  with a cathodic current yield of 23%. A non-structured hard chromium layer was obtained.

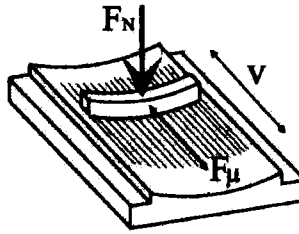
### Experiment 5

A chromium electrolyte having the following composition was prepared:

Chromium acid anhydride ( $\text{CrO}_3$ ):	250 g/L
Sulphuric acid ( $\text{H}_2\text{SO}_4$ ):	2.5 g/L
Ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ ):	100 g/L
Methane sulfonic acid:	4 g/L
Fluoride ( $\text{F}^-$ ), added as KF:	0.5 g/L

A piston ring was introduced into the electrolyte after conventional pre-treatment and electrolytically coated for 30 minutes at  $55^\circ\text{C}$  with a cathodic current yield of 11 %. A non-structured hard chromium layer was obtained.

2. Afterwards, the relative wear resistance and the seizure resistance of the coated piston rings obtained according to Experiments 1 – 5 were determined by a Rig test (heatable Rig tester of the company Plint). The Rig tester moves a part of a piston ring over a part of a cylinder wall in an oscillating manner. The frequency and the stroke of the movement determine the relative velocity of the piston ring and the cylinder wall:



Conditions:

Measurement of the wear resistance: 23 h,  $F_N$  (load) = 450 N,  $T = 190\text{ }^{\circ}\text{C}$ ,  $f$  (frequency) = 10 Hz,  $S$  (stroke) = 30 mm, ring diameter  $\varnothing = 78.3$  mm.

Measurement of the seizure resistance:  $F_N$  (load) = 30 - 800 N, load enhancement = 20 N/5 min, termination at  $\mu = 0.3$ ,  $T = 120\text{ }^{\circ}\text{C}$ ,  $f$  (frequency) = 40 Hz,  $S$  (stroke) = 4 mm, piston ring diameter  $\varnothing = 78.3$  mm.

In order to compare the wear resistance and the seizure resistance, the coated piston ring according to Experiment 1 was given a value of 100%. A higher percentage indicates a higher wear resistance and the seizure resistance, respectively.


3. The results are shown in the following table:

	Structure of the hard chromium coat	Wear Resistance	Seizure Resistance
Experiment 1	structured	100 %	100 %
Experiment 2	non-structured	50 – 70 %	50 – 70 %
Experiment 3	non-structured	50 – 70 %	50 – 70 %
Experiment 4	non-structured	50 – 70 %	50 – 70 %
Experiment 5	non-structured	50 – 70 %	50 – 70 %

4. The above data shows that cathodic current yields above 12% or the addition of fluoride give hard chromium coatings which do not have the desired structure and, consequently, have a significant lower wear resistance and seizure resistance. Therefore, there is a significant

improvement of the hard chromium coatings prepared according to present claimed invention compared to hard chromium coatings of the prior art.

Executed this 22 day of July, 2009



---

Rudolf Linde